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Entropy: Order or Information

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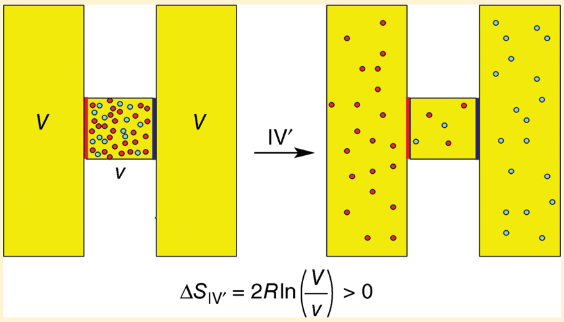
ABSTRACT: Changes in entropy can *sometimes* be interpreted in terms of changes in disorder. On the other hand, changes in entropy can *always* be interpreted in terms of changes in Shannon's measure of information. Mixing and demixing processes are used to highlight the pitfalls in the association of entropy with disorder.

KEYWORDS: First-Year Undergraduate/General, Upper-Division Undergraduate, Physical Chemistry, Misconceptions/Discrepant Events, Thermodynamics



In 1865, Rudolf Clausius introduced the concept of entropy in connection with his work on the mechanical theory of heat. The original definition of entropy in terms of heat transferred and absolute temperature did not offer and, in principle, could not offer any *molecular* interpretation of the entropy. Ludwig Boltzmann suggested an alternative definition of entropy in 1877 in terms of the number of microstates comprising a given macrostate. Boltzmann's definition opened the door to a molecular interpretation of entropy. Boltzmann stated:[1]

> *When this is the case, then whenever two or more small parts of it come into interaction with each other, the system formed by these parts is also initially in an ordered state, and when left to itself it rapidly proceeds to the disordered most probable state.*

Note that Boltzmann used the terms disorder and probability almost as synonyms. Both of these concepts are related to the number of microstates; the larger the number of microstates, the larger is the disorder, and the larger is the probability of the state.

The interpretation of *entropy* as *disorder* has prevailed in the literature for over 100 years.[2−4] It is true that many spontaneous processes may be viewed as proceeding from an ordered to a disordered state. However, there are two difficulties with this interpretation. First, the concept of order is not well-defined, and in many processes it is difficult, if not impossible, to decide which of the two states of the system is more or less ordered.[4−6] Some specific examples are provided in refs 4 and 6. Note however that the term disorder here is used in its colloquial sense. There are some specific systems for which an "order parameter" may be defined, but this is not the type of order discussed in describing entropy. Second, there are cases in which an increase in disorder is clearly observed, yet the entropy change can be either zero or negative, therefore, invalidating the interpretation of entropy in terms of order and disorder (see below). In spite of these difficulties, the order−disorder interpretation still lingers in the literature.[2,3]

In this article, a few processes involving mixing and demixing of ideal gases are presented. It is shown that the qualitative association of entropy changes with changes in order is, in general, invalid. Instead, the same processes can be consistently interpreted in terms of changes in the amount of missing information.[6]

Consider the following chain of reasoning that appears quite frequently in textbooks on thermodynamics:

(i) Mixing of two (or more) different ideal gases is a process that causes an *increase* in disorder.
(ii) Increase in disorder results in an *increase* in entropy.
(iii) It follows from i and ii that mixing of different ideal gases should be associated with an increase in entropy.

Statement iii, or some variations of it, appears in almost all textbooks of thermodynamics and statistical mechanics. As a consequence of this conclusion, most textbooks add the statement that *mixing of different ideal gases is an inherently irreversible process*.

The fallacy of this conclusion has been discussed in great detail more than 20 years ago.[5,6] Here, I demonstrate how the fallacy of this conclusion results from the association of entropy with disorder. I do this by means of a few examples shown in Figures 1−3. In all of these processes, we are not interested in the *actual* process leading from the initial to the final state, but only in the *difference* in the entropy of the system between the initial and the final states. All the processes described may be performed quasi-statically at constant temperature.[2] Because the systems contain only ideal gases, constant temperature also implies constant average kinetic energy of the particles.

■ EXAMPLES

Consider the three processes shown in Figure 1. In these processes we start with N molecules of one kind and N molecules of a second kind and end having the two different gases mixed in a volume V. Although there exists no precise definition of order or

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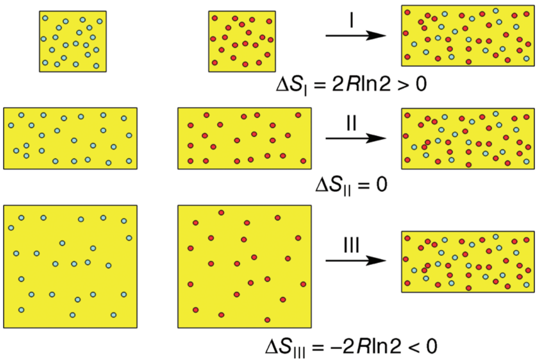

Figure 1. Three processes of mixing. The final states are the same in these processes; however, the entropy changes are different.

disorder, we feel intuitively that the *mixing* of two things, whether two different gases or mixing apples and oranges, is a *disordering* process. Therefore, statement i is qualitatively and intuitively accepted as correct.

Statement ii is commonly accepted as part of the interpretation of entropy as a measure of disorder. Even Gibbs used the term *mixedupness* in connection with his analysis of the entropy of mixing.[7] Clearly, it is not possible to check the validity of the second statement, qualitatively or quantitatively, because we do not have a precise measure of order or disorder. Instead, we can check the validity of statement iii and indirectly infer from it on the validity of statement ii. To do this, we calculate the entropy change either by classical thermodynamics or by statistical mechanics for the three processes. The results are well-known,[6]

$$\Delta S_{\text{I}} = 2R\ln 2 > 0 \tag{1}$$

$$\Delta S_{\text{II}} = 0 \tag{2}$$

$$\Delta S_{\text{III}} = -2R\ln 2 < 0 \tag{3}$$

where R is the gas constant. Note that in these processes, we are not concerned with the path leading from the initial to the final state; we are only interested in is the *difference* in entropy between the initial and the final states.

Clearly, these results are in conflict with statement iii, that is, in all the processes in Figure 1 we observe *mixing*, but the entropy change is either positive, zero, or negative. Because we have agreed that statement i is qualitatively and intuitively correct, we must conclude that statement ii is incorrect. Thus, we conclude that increase in disorder cannot, in general, be associated with increase in entropy. This association is sometimes correct, as for process I, but incorrect for processes II and III (Figure 1).

Before analyzing the psychological reasons for the commonly held view that associates mixing with disorder and before suggesting an alternative interpretation of the quantitative results in eqs 1−3, let us discuss another conclusion often stated in textbooks on thermodynamics, *namely that mixing of different ideal gases is an inherently spontaneous irreversible process.*[3,8] To see the fallacy of the latter statement, consider the two processes I and IV shown in Figure 2. For both of these processes the entropy change can be calculated:

$$\Delta S_{\text{I}} = 2R\ln 2 > 0 \tag{4}$$

$$\Delta S_{\text{IV}} = 2R\ln 2 > 0 \tag{5}$$

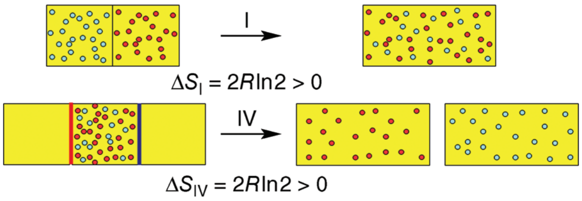

Figure 2. Two processes involving *positive* change in entropy. In process I, mixing occurs, but in process IV, demixing occurs.

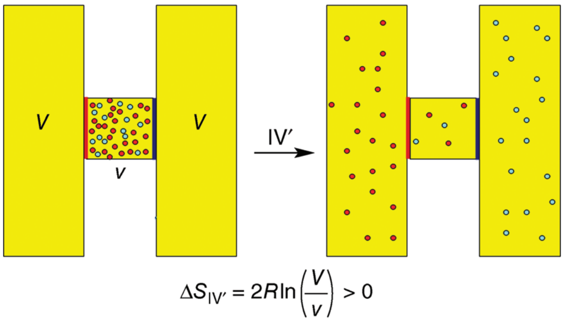

Figure 3. A process, IV′, in which almost complete demixing occurs spontaneously.

Process I can be carried out spontaneously simply by removing the partition separating the two gases. Process IV can be performed by utilizing semipermeable partitions, in two steps; one spontaneous, involving partial demixing with $\Delta S = 2R\ln 2$, followed by a reversible demixing of the remaining mixture.[3,5] Here, the terms reversible and irreversible are employed in the sense used by Callen,[2] that is, when the entropy of the system does not change and when it increases, respectively. The term quasi-static is used to describe a process carried out along an infinite sequence of equilibrium states.[2]

If one concludes, on the basis of process I, that *mixing* is a spontaneous *irreversible* process, one must also conclude from the result in process IV, eq 5, that *demixing* is a spontaneous *irreversible* process. Clearly, these two conclusions cannot be both correct. In fact they are both wrong, neither mixing nor demixing of ideal gases, in themselves, affect any thermodynamic quantity. Therefore, mixing was dubbed to be a thermodynamic nonprocess.[5]

Why do most textbooks on thermodynamics claim that mixing is an irreversible process and that mixing involves increase in entropy? The probable answer is that in daily life we see many mixing processes that are spontaneous. A drop of ink dropped into a glass of water will mix with the water, and we never see the reversal of these process. Processes similar to process I in Figure 2 are spontaneous and irreversible.

Admittedly, demixing processes that occur spontaneously are rare, but they do occur. If one vigorously mixes water with oil and let it settle, the two liquids will demix spontaneously. Another example is shown in Figure 3 that is essentially the same as process IV. We start with mixture of A and B in a small volume v. We then open two semipermeable partitions, one partition that allows A to pass but not B, and the second partition that allows B to pass but not A. If the volume V is much larger than volume v, we shall observe a spontaneous irreversible demixing of most of the mixture. The process of the demixing can be completed by reversibly moving the two partitions toward each other.[6] Note again that in the process of Figure 3, we are considering a demixing of ideal gases. Such processes are rare. However, when intermolecular interactions exist, one can devise many processes in which demixing occurs, for example see Chapter 6 in ref.[6]

If we show process IV′ to a student who has just learned that mixing is an irreversible process, he or she will almost certainly react by claiming that what we have done in process IV′ is simply *expansion* of the gas from a small to a large volume and that this expansion is the driving force for the irreversible process and the cause of the increase of entropy. The demixing has nothing to do with the increase of entropy. This explanation is correct. Indeed, the demixing in this process has nothing to do with the increase in entropy; this is simply a process of expansion! However, this is also true for the mixing process denoted I in Figure 1. It is the *expansion* rather than the *mixing* that drives process I, that is, the expansion of each gas from V to $2V$.

Thus, the correct conclusion from the observation of processes I and IV′ is not that the mixing or demixing is irreversible, but that in both processes the expansion is the driving force and the cause of the increase in entropy. While in one process we observe mixing and in the other process we observe demixing, neither mixing nor demixing has any effect on the entropy change in the process.[5,6]

Gibbs,[7] who probably was the first scientist to analyze the thermodynamics of mixing, was apparently more puzzled by the fact that the entropy of mixing of the two different gases is independent of the type of gases, than by the fact that when mixing two gases of the same kind, there is no change in entropy. Yet it seems that Gibbs failed to see that in process I, which he referred to as a “mixing of gases of different kinds”, is simply an expansion process and that the mixing in this process is only incidental.

Realizing that process I is just an expansion, there is no puzzlement. The change in entropy associated with the expansion process is independent of the kind of gas. The entropy change is simply the result of the increase in the accessible volume for each particle, from V to $2V$. Clearly, this entropy change must be independent of the type of gas that is expanding.

MEASURE OF INFORMATION

This brings us to the alternative interpretation of entropy change in terms of Shannon’s measure of information.[9,10] As we have seen, the incorrect conclusion reached in statement iii is due to the association of entropy with disorder. This conclusion would not have been reached had we associated the entropy with Shannon measure of information.[6,9,10] The fact that the order—disorder interpretation still lingers in the literature, in spite of the superiority of the informational interpretation, results because the concept of information is very general and encompasses both subjective and objective types of information. Only one measure of the amount of information as defined by Shannon[9] is relevant to the interpretation of the entropy.[5,10] The Shannon measure of information (SMI) is discussed in detail in ref 6. It is enough to say here that, for all the processes described in this article, the change in SMI is identical with the change in the thermodynamic entropy, except for the multiplicative Boltzmann constant; that is, the change in the SMI is simply $\ln(V_2/V_1)$, whereas the change in entropy is $k_B \ln(V_2/V_1)$. The informational interpretation of the change in entropy is provided by the SMI.

In all the processes discussed in this article, only the *accessible volume* for each particle has been changed. Because we are dealing with ideal gases, the change in volume does not involve a change in the velocity distribution, that is, no change in the velocity (or momentum) information. The only change we observe is the change in the *locational information*.[6,10]

Qualitatively, having a particle in a box of volume V, we can always divide the box into M small cells each of size v. The SMI may be defined as the number of binary questions one needs to ask to find the *location* of the particle. It is easy to show that, although the SMI depends on the size of the cells, the change in the SMI does not.[5] What matters is only the change in the number of cells M, from the initial to the final state. It can be shown that in the limit of very small size cells the change of the SMI, similar to the change in entropy is proportional to the logarithm of the ratio of the volumes in the two states.[6] In terms of locational SMI, we can interpret the four processes in Figures 1−3 as follows:

1. In process I, the accessible volume per particle *increases*; hence, the SMI *increases*.
2. In process II, the accessible volume per particle does not change; hence, no change in the SMI.
3. In process III, the accessible volume per particle *decreases*; hence, the SMI *decreases* too.
4. Similarly, in both processes I and IV′, there is an *increase* in SMI due to the increase in the accessible volume.

Thus, in process I and IV′ the entropy increases, in process II the entropy is constant, and in process III the entropy decreases. In all of these processes, mixing is observed but the mixing is inconsequential. Therefore, we did not deem it necessary to mention mixing, order, or disorder in the four statements made above.

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